(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 957 132 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.11.1999 Bulletin 1999/46

(21) Application number: **99303721.7**

(22) Date of filing: **12.05.1999**

(51) Int Cl.[6]: **C08L 77/00**, C08L 77/12, C08L 77/06, C08K 5/092 // (C08L77/00, 77:12)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **12.05.1998 JP 12935298**

(71) Applicant: **TORAY INDUSTRIES, INC.**
Tokyo 103-8666 (JP)

(72) Inventors:
- **Umetsu, Hideyuki**
Nagoya-shi, Aichi, 458-0044 (JP)
- **Sugimura, Masahiro**
Mizuho-ku, Nagoya-shi, Aichi 467-0042 (JP)
- **Makabe, Yoshiki**
Nagoya-shi, Aichi, 458-0821 (JP)

(74) Representative: **Coleiro, Raymond et al**
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) **Polyamide resin composition**

(57) A polyamide resin composition comprised 100 parts by weight of a polyamide resin, from 0.01 to 100 parts by weight of a liquid-crystalline resin, and from 0.01 to 5 parts by weight of an acid anhydride.

A box-type molding with thin-wall parts which account for at least 10% of the total surface area can be molded from such a composition.

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Description

[0001] The present invention relates to a polyamide resin composition and its moldings. The advantages of the composition are that, while dwelling in mold cylinders, it keeps good fluidity, that the amount of cushion resin needed for molding the composition fluctuates little, and that failures such as cobwebbing in molding the composition are reduced; and the advantages of the moldings of the composition are that they have good impact resistance and good outward appearance.

[0002] Since they have good mechanical properties, good abrasion resistance, good electric properties, good chemical resistance and good workability, polyamide resins such as typically nylon 6 and nylon 66 are widely used as engineering plastics in various fields, for example, in the field. of automobiles, in the field of electrical and electronic appliances and in other fields of building materials, sundries, etc.

[0003] High-quality plastics for many applications are much needed in those fields, and improving the quality of plastics is therefore much desired. For example, in the field of automobiles, it is desired to reduce as much as possible the destruction of the environment owing to exhaust gas. For this, automobile parts are being made in smaller sizes and with thinner walls so as to produce lightweight and compact cars. On the other hand, in the field of electrical and electronic appliances, portable personal computers are now popular, and housings for them are desired to be lightweight. At present, polyamide resins are used for the applications in those fields, and it is desired to further reduce the wall thickness of the moldings of polyamide resins. For this, the fluidity of polyamide resins must be improved.

[0004] In that situation, a large number of polymers having various novel characteristics have been developed and put on the market. Of those, optically-anisotropic, liquid-crystalline polymers characterized by the parallel orientation of molecular chains are of specific note as having high fluidity and good mechanical properties. In particular, as the polymers of those types have especially high strength and stiffness, there is a considerably increasing demand for small-sized moldings of such polymers in the field of electrical engineering and electronics and also in the field of office appliances. Various techniques of mixing the two different resins, liquid-crystalline resin and thermoplastic resin, have heretofore been proposed so as to obtain resin mixtures having good characteristics of the two resins, for example, as in JP-A-56-115357, JP-A-01-259062, JP-A-054222, JP-A-05-086286 and JP-A-09-012875.

[0005] However, merely mixing the two polymers could not produce significant improvements in the physical properties of the resulting mixture, since the two polymers do not have good compatibility with each other. Because of their poor compatibility, either one of the two polymers is to be a foreign impurity component in the mixture of the two, whereby the impact strength of the moldings of the mixture is lowered. In addition, it has been found that, when the mixture is molded in a large-sized molding machine, it often undergoes amide-ester interaction owing to the long residence time in the mold. As a result, the fluidity of the mixture in the mold is rather lowered, contrary to the intended object of increasing the fluidity of resin mixtures. JP-A-09-012875 discloses a resin composition comprising a specific, terminal-blocked polyamide and a liquid-crystalline resin. In this, they say that monocarboxylic acids and acid anhydrides are usable as the terminal-blocking agent for the polyamide. Specifically, the invention disclosed is to blend a polyamide and a liquid-crystalline resin in a simple ordinary mixing manner, in which the polyamide is terminal-blocked during its polymerization so as to retard the interaction with the liquid-crystalline resin in the resulting mixture. In the disclosed method, however, the compatibility of the two polymers is still poor, and the physical properties of the resulting mixture of the two polymers are inevitably degraded. We, the present inventors tried the method, using a large-sized molding machine for producing large-sized moldings, and, as a result, have found that, since the resin mixture inevitably dwells in the cylinder, it decomposes or foams and even its viscosity increases. In our experiment, therefore, the fluidity of the resin mixture rather lowered. It is believed that the phenomenon of the viscosity increase to lower the fluidity of the resin mixture will be because of the amide-ester interaction having occurred between the two resins in the mixture.

[0006] The invention addresses the problem of providing a polyamide resin composition capable of being worked at temperatures at which conventional polyamide resins are worked. Other problems solved by the composition are that the composition does not lose good characteristics intrinsic to ordinary polyamide resins, that it keeps good fluidity all the time even when it stays in mold cylinders so as to be molded into moldings having specific morphology, that the amount of cushion resin needed for molding the composition fluctuates little, that failures such as cobwebbing in molding the composition are reduced, and that the moldings of the composition have good impact resistance and good outward appearance.

[0007] The invention provides a polyamide resin composition comprising 100 parts by weight of a polyamide resin, from 0.01 to 100 parts by weight of a liquid-crystalline resin, and from 0.01 to 5 parts by weight of a polycarboxylic acid anhydride component.

[0008] In formulating such a composition, for example, prior to molding, the anhydride component may react with other components of the mixture, whereby at least a portion of the carboxylic acid anhydride component is present in at least one other component of the resin. Such a composition lies within the invention. As regards weight basis, the units in the other components derived from the anhydride are not to be regarded as part of the content of the other components, but as part of the anhydride content.

[0009] Thus, according to another aspect, the invention provides a polyamide resin composition obtainable by mixing, in molten form,100 parts by weight of a polyamide resin, from 0.01 to 100 parts by weight of a liquid-crystalline resin, and, in molten or liquid form, from 0.01 to 5 parts by weight of a polycarboxylic acid anhydride.

[0010] Preferred embodiments of the invention are mentioned below.

[0011] In a composition embodying the invention, the liquid crystal transition temperature of the liquid-crystalline resin is preferably not higher than the melting point of the polyamide resin.

[0012] The composition may additionally contain a filler in an amount of from 0.5 to 300 parts by weight relative to 100 parts by weight of the sum total of the polyamide resin, the liquid-crystalline resin and the acid anhydride.

[0013] In the composition, the melt viscosity of the liquid-crystalline resin is preferably not higher than 50 Pa·s, as measured at a temperature of the melting point of the polyamide resin + 25°C and at a shear rate of 1000 sec^{-1}.

[0014] In the composition, the acid anhydride is preferably a dicarboxylic acid anhydride and is preferably aromatic. Most preferably, the acid anhydride is at least one selected from succinic anhydride, 1,8-naphthalic anhydride, phthalic anhydride and maleic anhydride.

[0015] A box-type molding in accordance with the invention has thin-wall parts of the polyamide resin composition, in which the thin-wall parts having a thickness of at most 1.0 mm account for at least 10% of the total surface area of the molding.

[0016] Preferred embodiments of the invention are now described in in detail. "weight" as referred to herein indicates "mass".

[0017] The polyamide resin for use in the invention may be a nylon prepared from starting materials of an amino acid, a lactam or a diamine, and a dicarboxylic acid. Specific examples of the starting materials include amino acids such as 6-aminocaproic acid, 11-aminoundecanoic acid, 12-aminododecanoic acid and paraaminomethylbenzoic acid, lactams such as ε-aminocaprolactam and ω-laurolactam, aliphatic, alicyclic or aromatic diamines such as tetramethylenediamine, hexamethylenediamine, 2-methylpentamethylenediamine, nonanemethylenediamine, undecamethylenediamine, dodecamethylenediamine, 2,2,4-/2,4,4-trimethylhexamethylenediamine, 5-methylnonamethylenediamine, metaxylenediamine, paraxylylenediamine, 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane, bis(4-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, bis(aminopropyl)piperazine and aminoethylpiperazine aliphatic, alicyclic or aromatic dicarboxylic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, dodecane-diacid, terephthalic acid, isophthalic acid, 2-chloroterephthalic acid, 2-methylterephthalic acid, 5-methylisophthalic acid, 5-sodium-sulfoisophthalic acid, hexahydroterephthalic acid and hexahydroisophthalic acid. In the invention, nylon homopolymers or copolymers to be derived from those starting materials may be used herein either singly or as mixtures thereof.

[0018] Nylon resins with good heat resistance and strength, having a melting point of not lower than 200°C, are especially preferred as the polyamide resin for use in the invention. As their specific examples, mentioned are polycapramide (nylon 6), polyhexamethylenadipamide (nylon 66), polytetramethylenadipamide (nylon 46), polyhexamethylenesebacamide (nylon 610), polyhexamethylenedodecamide (nylon 612), polynonanemethyleneterephthalamide (nylon 9T), polyhexamethylenadipamide/polyhexamethyleneterephthalamide copolymer (nylon 66/6T), polyhexamethyleneterephthalamide/polycapramide copolymer (nylon 6T/6), polyhexamethylenadipamide/polyhexamethylenisophthalamide copolymer (nylon 66/6I), polydodecamide/polyhexamethyleneterephthalamide copolymer (nylon 12/6T), polyhexamethylenadipamide/polyhexamethyleneterephthalamide /-polyhexamethylenisophthalamide copolymer (nylon 66/6T/6I), polyhexamethyleneterephthalamide/polyhexamethylenisophthalamide copolymer (nylon 6T/6I), polyhexamethyleneterephthalamide/poly(2-methylpentamethyleneterephthalamide) copolymer (nylon 6T/MST), polyxylylenadipamide (nylon XD6), as well as mixtures and copolymers thereof.

[0019] Especially preferred are nylon 6, nylon 66, nylon 610, nylon 46, nylon 9T, nylon 6/66 copolymer, nylon 6/12 copolymer, nylon 9T, nylon 6T/6 copolymer, nylon 66/6T copolymer, nylon 6T/6I copolymer, nylon 66/6T/6I copolymer, nylon 12/6T copolymer and nylon 6T/MST copolymer. Practically, it is often preferable to use these nylon resins in the form of mixtures thereof, depending on the desired characteristics such as moldability, heat resistance and water absorption resistance of the resins.

[0020] Preferably, the degree of polymerization of the polyamide resin for use in the invention is such as to provide a relative viscosity of the resin, as measured in a solution of concentrated sulfuric acid to have a resin concentration of 1 5, at 25°C, of from 1.5 to 5.0, more preferably from 2.0 to 4.0, inclusive.

[0021] The terminal amino content of the polyamide resin for use in the invention is preferably at most 100 x 10^{-6} equivalents/g, more preferably at most 70 x 10^{-6} equivalents/g, even more preferably at most 50 x 10^{-6} equivalents/g.

[0022] A method for measuring the terminal amino content of the polyamide resin for use in the invention is as follows. A 20 mg sample is weighted in an NMR sample tube, dissolved in 0.6 ml of a solvent (hexafluoroisopropanol-d'2) added thereto, and subjected to NMR spectrometry at a frequency of 599.9 MHz.

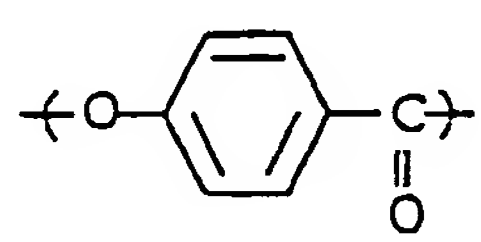
[0023] The liquid-crystalline resin for use in the invention is one capable of forming an anisotropic melt phase. For example, it includes liquid-crystalline polyesters comprising structural units that are selected from aromatic oxycarbonyl units, aromatic dioxy units, aromatic dicarbonyl units and ethylenedioxy units aromatic dicarbonyl units and anisotropic

units and capable of forming an anisotropic melt phase; liquid-crystalline polyesteramides comprising structural units selected from those mentioned above, along with other structural units that are selected from aromatic iminocarbonyl units, aromatic diimino units and aromatic iminoxy units and capable of forming an anisotropic melt phase.

[0024] The aromatic oxycarbonyl units include, for example, structural units derived from p-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid; the aromatic dioxy units include, for example, those from 4,4'-dihydroxybiphenyl, hydroquinone, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl, t-butylhydroquinone, phenylhydroquinone, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2,2-bis(4-hydroxyphenyl)propane and 4,4'-dihydroxydiphenyl ether the aromatic dicarbonyl units include, for example, those from terephthalic acid, isophthalic acid, 2,6-naphthalene-dicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 1,2-bis(phenoxy)ethane-4,4'-dicarboxylic acid, 1,2-bis(2-chlorophenoxy)ethane-4,4'-dicarboxylic acid and 4,4'-diphenyl ether-dicarboxylic acid; the aromatic iminoxy units include, for example, those from 4-aminophenol.

[0025] Specific examples of the liquid-crystalline polyesters are liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzoic acid, those from 6-hydroxy-2-naphthoic acid, and those from aromatic dihydroxy compounds and/or aliphatic dicarboxylic acids; liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzoic acid, those from 4,4'-dihydroxybiphenyl, and those from terephthalic acid and adipic acid; liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzoic acid, those from aromatic dihydroxy compounds such as 4,4'-dihydroxybiphenyl and hydroquinone and those from terephthalic acid and/or 2,6-naphthalene-dicarboxylic acid; liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzoic acid, those from ethylene glycol, and those from terephthalic acid and isophthalic acid; liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzbic acid, those from ethylene glycol, those from 4,4'-dihydroxybiphenyl, and those from terephthalic acid and/or sebacic acid; liquid-crystalline polyesters comprising structural units derived from p-hydroxybenzoic acid, those from ethylene glycol, those from aromatic dihydroxy compounds, those from aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid and 2,6-naphthalene-dicarboxylic acid.

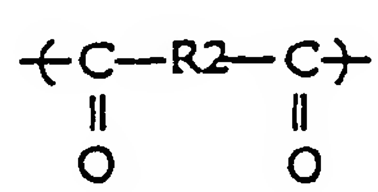
[0026] Preferred examples of the liquid-crystalline polyesters capable of forming an anisotropic melt phase are liquid-crystalline polyesters comprising structural units of the following (I), (II), (III) and (IV), and liquid-crystalline polyesters comprising structural units of the following (I), (III) and (IV) and capable of forming an anisotropic melt phase.



(I)

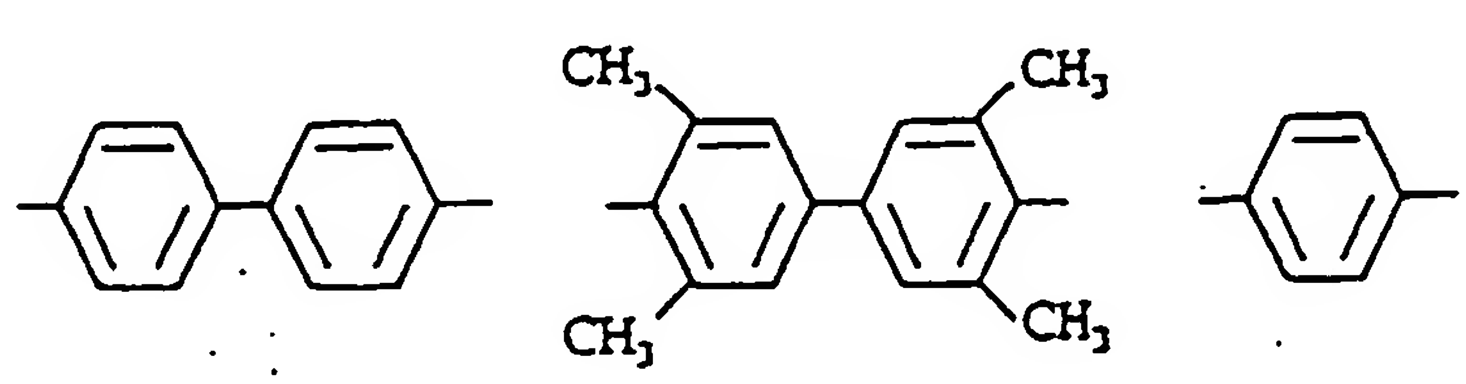
$$\{O\text{-}R1\text{-}O\} \qquad (II)$$

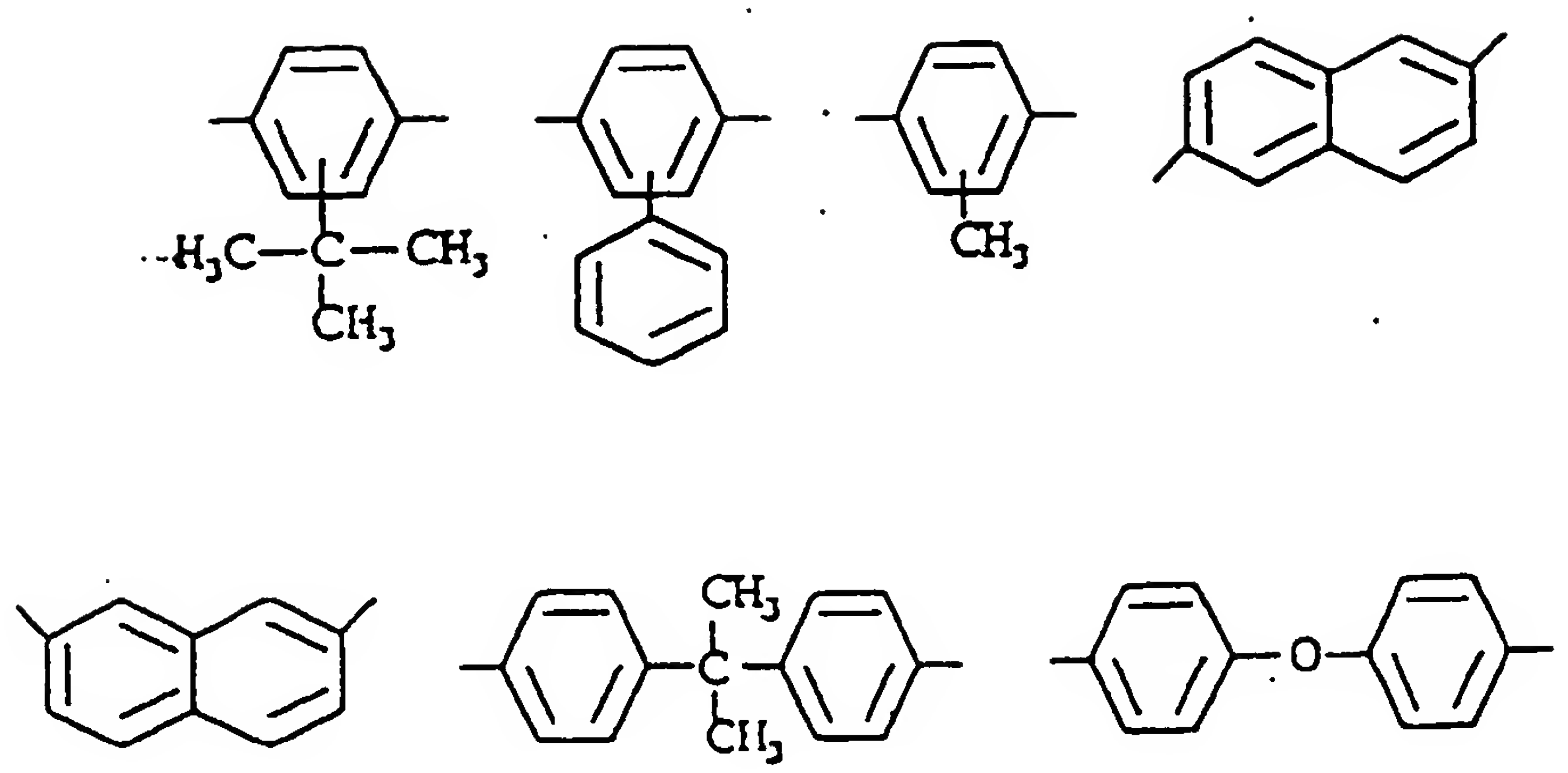
$$\{O\text{-}CH_2CH_2\text{-}O\} \qquad (III)$$



(IV)

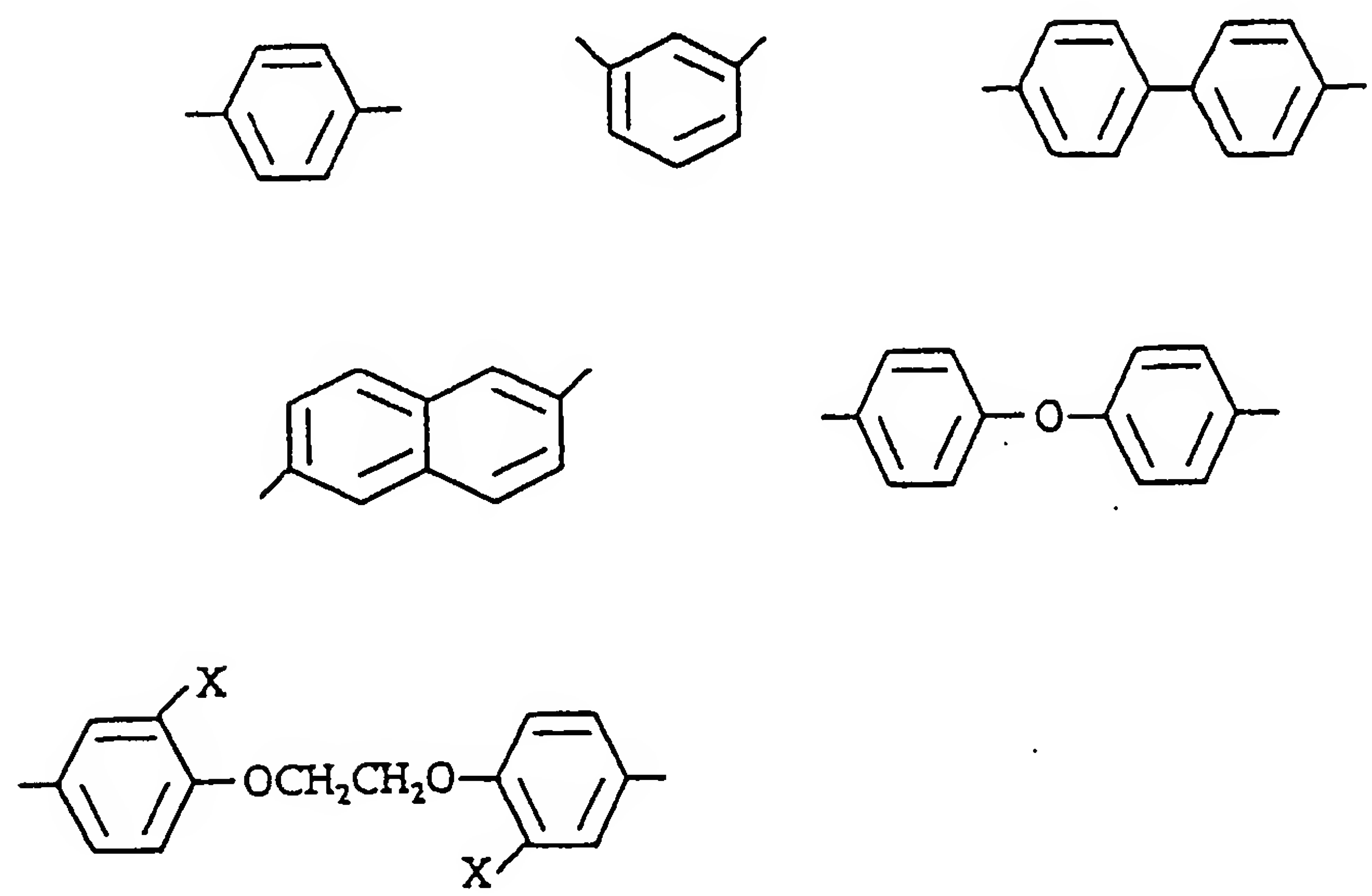
wherein R_1 represents one or more groups selected from the following:





;

R_2 represents one or more groups selected from the following:



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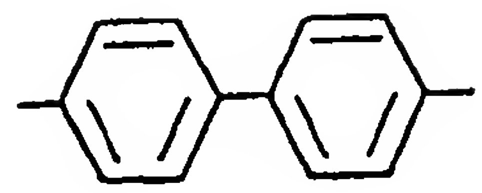
X represents a hydrogen atom or a chlorine atom.

[0027] The structural unit (I) is derived from p-hydroxybenzoic acid; the structural unit (II) is from at least one aromatic dihydroxy compound selected from 4,4'-dihydroxybiphenyl, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl, hydroquinone, t-butylhydroquinone, phenylhydroquinone, methylhydroquinone, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2,2-bis(4-hydroxyphenyl)propane and 4,4'-dihydroxydiphenyl ether; the structural unit (III) is from ethylene glycol; and the structural unit (IV) is from at least one aromatic dicarboxylic acid selected from terephthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 2,6-naphthalene-dicarboxylic acid, 1,2-bis(phenoxy)ethane-4,4'-dicarboxylic acid, 1,2-bis(2-chlorophenoxy)ethane-4,4'-dicarboxylic acid and 4,4'-diphenyl ether-dicarboxylic acid.

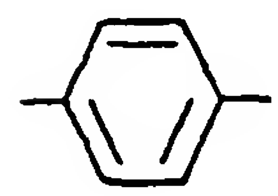
[0028] Of the structural units mentioned above, especially preferred are those where R_1 is the following:

[4]



[0029] Also preferably, R_2 is the following:

[5]



[0030] Preferred liquid-crystalline polyesters for use in the invention are the copolymers comprising the structural units (I), (III) and (IV), and the copolymers comprising the structural units (I), (II), (III) and (IV), in which the copolymerizing ratio of those units (I), (II), (III) and (IV) may be freely defined. However, in order to obtain good results of the invention, the copolymerizing ratio is preferably as follows:

[0031] In the copolymers comprising the structural units (I), (III) and (IV), the structural units (I) are preferably from 30 to 80 mol%, more preferably from 45 to 75 mol% of the total of the structural units (I), (III) and (IV).

[0032] In the copolymers comprising the structural units of (I), (II), (III) and (IV), the total of the structural units (I) and (II) is preferably from 30 to 95 mol%, more preferably from 40 to 85 mol% of the total of the structural units (I), (II) and (III). The structural units (III) are preferably from 5 to 70 mol%, more preferably from 15 to 60 mol% of the total of the structural units (I), (II) and (III). The molar ratio of the structural units (I) to (II), i.e. (I)/(II), is preferably from 75/25 to 95/5, more preferably from 78/22 to 93/7. Preferably, the structural units (IV) are substantially equimolar to the total of the structural units (II) and (III).

[0033] Liquid-crystalline polyester-amides are also usable in the invention. Preferably, these comprise p-iminophenoxy units to be derived from p-aminophenol, in addition to the structural units (I) to (IV) noted above, and are capable of forming an anisotropic melt phase.

[0034] The liquid-crystalline polyesters and polyesteramides which are preferably used in the invention may comprise, in addition to the structural units (I) to (IV) mentioned above, any other structural units from comonomers of, for example, aromatic dicarboxylic acids such as 3,3'-diphenyldicarboxylic acid and 2,2'-diphenyldicarboxylic acid; aliphatic dicarboxylic acids such as adipic acid, azelaic acid, sebacic acid and dodecane-dicarboxylic acid; alicyclic dicarboxylic acids such as hexahydroterephthalic acid; aromatic diols such as chlorohydroquinone, 3,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxybenzophenone and 3,4'-dihydroxybiphenyl aliphatic and alicyclic diols such as propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol; aromatic hydroxycarboxylic acids such as m-hydroxybenzoic acid and 2,6-dihydroxynaphthoic acid; as well as, e.g., p-aminophenol and p-aminobenzoic acid, so far as the additional comonomer units do not interfere with the liquid-crystalline property of the copolymers.

[0035] The liquid-crystalline resins mentioned above for use in the invention can be produced in accordance with any known polycondensation methods for producing conventional polyesters.

[0036] For example, to produce the liquid-crystalline polyesters noted above, the following methods are preferred.

(1) A polyester is prepared from components except p-hydroxybenzoic acid, then this is heated and melted with p-acetoxybenzoic acid in a dry nitrogen stream atmosphere to form copolymerized polyester fragments through acidolysis, and thereafter the viscosity of the resulting copolyester is increased under reduced pressure.

(2) P-acetoxybenzoic acid, a diacylated, aromatic dihydroxy compound such as 4,4'-diacetoxybiphenyl or diacetoxybenzene, and an aromatic dicarboxylic acid such as 2,6-naphthalene-dicarboxylic acid, terephthalic acid or isophthalic acid are subjected to deacetylating polycondensation.

(3) P-hydroxybenzoic acid, an aromatic dihydroxy compound such as 4,4'-dihydroxybiphenyl or hydroquinone, an aromatic dicarboxylic acid such as 2,6-naphthalene-dicarboxylic acid, terephthalic acid or isophthalic acid, and acetic anhydride are subjected to acylation at the phenolic hydroxyl groups followed by deacetylating polycondensation.

(4) Phenyl p-hydroxybenzoate, an aromatic dihydroxy compound such as 4,4'-dihydroxybiphenyl or hydroquinone, and a diphenyl ester of an aromatic dicarboxylic acid such as 2,6-naphthalene-dicarboxylic acid, terephthalic acid or isophthalic acid are subjected to dephenolating polycondensation.

(5) P-hydroxybenzoic acid and an aromatic dicarboxylic acid such as 2,6-naphthalene-dicarboxylic acid, terephthalic acid or isophthalic acid are reacted with a predetermined amount of diphenyl carbonate to prepare a diphenyl ester, and then reacted with an aromatic dihydroxy compound such as 4,4'-dihydroxybiphenyl, hydroquinone for dephenolating polycondensation.

(6) The method of (2) or (3) is effected in the presence of a polymer or oligomer of a polyester such as polyethylene terephthalate, or in the presence of a bis(β-hydroxyethyl) ester of an aromatic dicarboxylic acid such as bis(β-hydroxyethyl) terephthalate.

[0037] The polycondensation for producing the liquid-crystalline resins may be effected in the absence of a catalyst, for which, however, a metal compound such as stannous acetate, tetrabutyl titanate, potassium acetate, sodium acetate or antimony trioxide, or even a metal of magnesium, may be used.

[0038] The logarithmic viscosity of the liquid-crystalline resin for use in the invention can be measured in pentafluorophenol, and is preferably not smaller than 0.03 g/dl when measured therein at a concentration of 0.1 g/dl at 60°C. More preferably, it is from 0.05 to 10.0 dl/g.

[0039] The liquid crystal transition temperature of the liquid-crystalline resin for use in the invention is preferably not higher than the melting point of the polyamide resin to be combined with it, more preferably not higher than the melting point of the polyamide resin - 10°C, even more preferably not higher than the melting point of the polyamide resin - 20°C. This is because the liquid-crystalline resin, of which the liquid crystal transition temperature is lower than the melting point of the polyamide to be combined with it, can uniformly disperse in the polyamide resin, and therefore produces better results in the invention.

[0040] To measure the liquid crystal transition temperature of the liquid-crystalline resin, a thin test piece of the resin is prepared, mounted on a sample stand of a polarization microscope and gradually heated thereon, whereupon the temperature at which the test piece emits milky light under shear stress is measured. Of most preferred liquid-crystalline resins for use in the invention, the liquid crystal transition temperature is lower by about 20°C or so than the melting point thereof. In order to obtain better results in the invention the melt viscosity of the liquid-crystalline resin, as measured at a temperature of the melting point of the polyamide resin to be combined with it + 25°C, is preferably not higher than 50 Pa·s, more preferably from 0.1 to 30 Pa·s, most preferably from 0.5 to 25 Pa·s. The melt viscosity is measured, using a vertical flow tester in which the sample is made to flow out through a nozzle having a diameter of 0.5 mmϕ and a length of 10 mm at a shear rate of 1,000 (1/sec).

[0041] In the composition of the invention, the amount of the liquid-crystalline resin to be added to the polyamide resin is from 0.01 to 100 parts, but preferably from 0.05 to 80 parts by weight, more preferably from 0.1 to 10 parts by weight, relative to 100 parts by weight of the polyamide resin. Within the defined range, the liquid-crystalline resin added does not interfere with the intrinsic characteristics of the polyamide resin, and the resulting resin composition can have various additional advantages. For example, the composition has good fluidity, the amount of cushion resin needed for molding the composition fluctuates little, the failures such as cobwebbing in molding the composition are reduced, and the moldings of the composition have good impact resistance and good outward appearance.

[0042] The acid anhydride in the composition of one invention includes, for example, benzoic anhydride, isobutyric anhydride, itaconic anhydride, octanoic anhydride, glutaric anhydride, succinic anhydride, acetic anhydride, dimethylmaleic anhydride, decanoic anhydride, trimellitic anhydride, 1,8-naphthalic anhydride, phthalic anhydride or maleic anhydride. Of those, preferred are succinic anhydride, 1,8-naphthalic anhydride, phthalic anhydride and maleic anhydride. More preferred are succinic anhydride and phthalic anhydride.

[0043] The amount of the acid anhydride to be added to the polyamide resin of the invention is from 0.01 to 5 parts by weight, but preferably from 0.05 to 3 parts by weight, more preferably from 0.1 to 2 parts by weight. If the amount of the acid anhydride added is too small, the resin composition does not have the advantages as above. For example, the composition does not have good fluidity. If the amount is too much, on the other hand, the composition will generate much gas while it is compounded or while it is molded. Owing to the gas, smooth filling of the composition into molds is often difficult, and, in addition, the moldings will be yellowed and will have many voids therein. Moreover, the moldings will have poor appearance, and their mechanical properties are degraded.

[0044] At least some of the acid anhydride existing in the polyamide resin composition of the invention need not be present in the final composition as the anhydride itself. For example, it may be in the composition in the form of the acid anhydride itself, or may be in any other form thereof as reacted, during formulation of the polyamide resin composition, with water or with the polyamide or liquid-crystalline resin or even with monomers or oligomers thereof.

[0045] In order to mix the polyamide resin, the liquid-crystalline resin and the acid anhydride to prepare the composition of the invention, in general, they are preferably kneaded in molten form. For the melt-kneading, any known method is employable. For example, the constituent components may be kneaded in molten form at a temperature falling between 180 and 380°C, with any of, for example, Banbury mixers, rubber rollers, kneaders, single-screw or double-screw extruders to give the resin composition of the invention. Preferably, however, they are mixed in extruders. For this, the order of mixing them is not specifically defined. preferably, the polyamide resin and the acid anhydride

are kneaded together. For example, the polyamide resin and the acid anhydride are first blended, to which is added the liquid-crystalline resin. When a two-stage extruder equipped with a side feeder is used, the former two are first blended therein and the liquid-crystalline resin is added to the resulting mixture via the side feeder. Also preferably, the polyamide resin, the liquid-crystalline resin and the acid anhydride may be blended all at a time.

[0046] A filler may be added to the polyamide resin composition of the invention for the purpose of further improving the characteristics of the composition, for example, for increasing the mechanical strength of composition. The filler is not specifically defined, and any of fibrous, tabular, powdery or granular fillers are employable herein. Specifically, the filler for use in the invention includes fibrous or whisker-like fillers, for example, glass fibers, carbon fibers of PAN, or pitch, metal fibers such as stainless steel fibers, aluminium fibers, or brass fibers, organic fibers such as aromatic polyamide fibers, as well as gypsum fibers, ceramic fibers, asbestos fibers, zirconia fibers, alumina fibers, silica fibers, titanium oxide fibers, silicon carbide fibers, rock wool, potassium titanate whiskers, barium titanate whiskers, aluminium borate whiskers and silicon nitride whiskers; and also other powdery, granular or tabular fillers of, for example, mica, talc, kaolin, silica, calcium carbonate, glass beads, glass flakes, glass microballoons, clay, molybdenum disulfide, wollastonite, titanium oxide, zinc oxide, calcium polyphosphate, or graphite. Of those fillers, preferred are glass fibers and carbon fibers. Especially preferred are PAN carbon fibers for making the composition have electroconductivity. The type of glass fibers for use in the Invention is not specifically defined, and any and every one generally used for reinforcing resins is employable herein. For example, they may be selected from long-fiber type or short-fiber type, chopped strands and milled fibers. Two or more of those fillers may be used in combination. The fillers for use in the invention may be surface-treated with any known coupling agents (e.g., silane coupling agents or titanate coupling agents, or any other surface-treating agents.

[0047] Glass fibers for use in the invention may be coated with a thermoplastic resin such as ethylene/vinyl acetate copolymer, or with a thermosetting resin such as epoxy resin, or may be bundled up therewith.

[0048] In general, the amount of the filler in the composition is preferably at most 300 parts by weight, but more preferably from 10 to 250 parts by weight, still more preferably from 20 to 150 parts by weight, relative to 100 parts by weight of the total amount of the polyamide resin, the liquid-crystalline resin and the acid anhydride.

[0049] A copper compound is preferably added to the polyamide resin composition of the invention so as to improve the long-term heat resistance of the composition. Specific examples of type copper compound include cuprous chloride, cupric chloride, cuprous bromide, cupric bromide, cuprous iodide, cupric iodide, cupric sulfate, cupric nitrate, copper phosphate, cuprous acetate, cupric acetate, cupric salicylate, cupric stearate, cupric benzoate, and complexes of an inorganic copper halide such as that mentioned above with, e.g. xylylenediamine, 2-mercaptobenzimidazole, or benzimidazole. Of those, monovalent copper compounds, especially monovalent copper halides, are preferred. Preferred examples of the compounds are,cuprous acetate and cuprous iodide. In preferably from 0.01 to 2 parts by weight, more preferably from 0.015 to 1 part by weight, relative to 100 parts by weight of the polyamide resin. If the amount is too large, free metal copper will segregate out in the melt of the composition being molded, whereby the moldings will be unfavorably colored to degrade their commercial value. In accordance with the invention as combined with the copper compound, an alkali halide may be added to the composition. Examples of the alkali halide are lithium chloride, lithium bromide, lithium iodide, potassium chloride, potassium, bromide, potassium iodide, sodium bromide and sodium iodide. Especially preferred are potassium iodide and sodium iodide.

[0050] Adding an alkoxysilane having at least one functional group selected from epoxy, amino, isocyanato, hydroxyl, mercapto and ureido groups, to the resin composition of the invention is preferred, for effectively improving the mechanical strength and the stiffness of the moldings of the composition. Specific examples of the alkoxysilane include epoxy-containing alkoxysilanes such as γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane ; mercapto-containing alkoxysilanes such as γ-mercaptopropyltrimethoxysilane and γ-mercaptopropyltriethoxysilane; ureido-containing alkoxysilanes such as γ-ureidopropyltriethoxysilane, γ-ureidopropyltrimethoxysilane and γ-(2-ureidoethyl)aminopropyltrimethoxysilane; isocyanato-containing alkoxysilanes such as γ-isocyanatopropyltriethoxysilane, γ-isocyanatopropyltrimethoxysilane, γ-isocyanatopropylmethyldimethoxysilane, γ-isocyanatopropylmethyldiethoxysilane, γ-isocyanatopropylethyldimethoxysilane, γ-isocyanatopropylethyldiethoxysilane, and isocyanatopropyltrichlorosilane, amino-containing alkoxysilanes such as γ-(2-aminoethyl)aminopropylmethyldimethoxysilane, γ-(2-aminoethyl)aminopropyltrimethoxysilane and γ-aminopropyltrimethoxysilane; hydroxyl-containing alkoxysilanes such as γ-hydroxypropyltrimethoxysilane and γ-hydroxypropyltriethoxysilane.

[0051] The resin composition of the invention may contain any ordinary additives, for example, antioxidants and heat stabilizers (e.g., hindered phenols, hydroquinones, phosphites and their substituted derivatives; ultraviolet absorbents (e.g., resorcinols, salicylates, benzotriazoles, benzophenones; coloration inhibitors such as phosphites, hypophosphites; lubricants and mold-release agents (e.g., montanic acid and its salts, esters and half-esters, stearyl alcohol, stearamides, polyethylene wax; colorants containing dye (e.g., Nigrosine) and pigment (e.g., cadmium sulfide, phthalocyanine); electroconductive agents and colorants such as carbon black; nucleating agents; plasticizers; flame retardants, (e.g., red phosphorus, magnesium hydroxide, melamine, cyanuric acid and its salts, poly-(styrene bromide), brominated polystyrene, polyphenylene ether bromides, brominated epoxy compounds, polycarbonate bromides; flame

retardation promoters (e.g., antimony compounds, fluorine resins, phenolic resins; and antistatic agents. Those additives may impart predetermined characteristics to the composition.

[0052] To add them to the resin composition, the inorganic filler and the additives mentioned above are preferably kneaded with the constituent components for the composition in melt. For the melt-kneading, any known method is employable. For example, using any of, for example, Banbury mixers, rubber rollers, kneaders, single-screw or double-screw extruders, they are kneaded with the constituent components in melt at a temperature falling between 180 and 380°C. Those additives may be added to the resin composition at any stage of preparing the composition by mixing the constituent components of the polyamide resin, the acid anhydride and the liquid-crystalline resin according to the preferred methods mentioned above. Specifically, the polyamide resin and the acid anhydride are first mixed in melt, to which the liquid-crystalline resin and the filler are added; or the components are all mixed at the same time; or the polyamide resin, the acid anhydride and the liquid-crystalline resin are first mixed, to which are added the filler and other additives; or the polyamide resin, the acid anhydride and the liquid-crystalline resin are first mixed to prepare a resin composition (A), and the resulting resin composition (A) is mixed with a filler to prepare a high-concentration composition (master) (B). Any of those methods are employable herein.

[0053] To produce moldings of the resin composition of the invention, any ordinary molding methods are employable, for example, injection molding, extrusion molding, blow molding, press molding or injection-press molding, in which are formed, e.g., three-dimensional moldings, sheets, containers or pipes. Since the composition has good fluidity, it is especially preferably molded into moldings having thin-wall parts (for example, tabular moldings or box-type moldings, but preferably box-type moldings), in particular into those with thin-wall parts having a thickness of not larger than 1.0 mm. Specifically, the composition is especially effectively molded into moldings with thin-wall parts, in which the thin-wall parts having a thickness of at most 1.0 mm account for at least 10 % of the total surface area of the molding, more preferably the thin-wall parts having a thickness of at most 1.0 mm account for at least 15 % of the same, even more preferably the thin-wall parts having a thickness of at most 0.8 mm account for at least 10 % of the same. For molding the composition into those moldings, preferred is a method of injection molding or injection-press molding.

[0054] As mentioned hereinabove, the polyamide resin composition of the invention has various novel advantages. Specifically, the composition does not lose good characteristics intrinsic to ordinary polyamide resins, and it keeps good fluidity all the time while it is molded. The producibility of maldings from the composition is good, in that the amount of cushion resin needed for molding the composition fluctuates little, and that failures such as cobwebbing in molding the composition are reduced. In addition, the moldings of the composition have good impact resistance and good outward appearance. Owing to its characteristics, therefore, the resin composition can be molded into various moldings. For example, the moldings are useful as parts for electrical and electronic appliances, such as typically various gears, various cases, sensors, LEP lamps, connectors, sockets, resistors, relay cases, switches, coil bobbins, capacitors, variable capacitor cases, optical pickups, oscillators, plates for various terminals, transformers, plugs, boards for printed circuits, tuners, speakers, microphones, headphones, small-sized motors, magnetic head bases, power modules, housings, semiconductors, parts for liquid crystal displays, FDD carriages, FDD chassis, HDD parts, motor brush holders, parabolic antannae and computer-related parts; parts for electric appliances for household and office use, such as typically VTR parts, TV parts, irons, hair driers, rice cooker parts, microwave range parts, acoustic parts, parts for sound appliances including audios, laser discs, and compact discs; lighting parts, refrigerator parts, air conditioner parts, typewriter parts and word processor parts; office computer-related parts, telephone-related parts, facsimile-related parts, duplicator-related parts, and washing tools; machine-related parts, such as typically various bearings including oilless bearings, stern bearings, and underwater bearings; motor parts, lighters, and typewriters; optical instrument-related parts and precision instrument-related parts, such as typically parts for microscopes, binoculars, cameras, and watches; automobile and vehicle-related parts, such as typically alternator terminals, alternator connectors, IC regulators, various valves including exhaust gas valves, various pipes for fuel-related intake and emission systems, air intake nozzle snorkels, intake manifolds, fuel pumps, engine-cooling water joints, carburetor main bodies, carburetor spacers, exhaust gas sensors, cooling water sensors, oil temperature sensors, brake pad wear sensors, throttle position sensors, crank shaft position sensors, air flow meters, thermostat bases for air conditioners, air flow control valves for heaters, brush holders for radiator motors, water pump impellers, turbine veins, wiper motor-related parts, distributors, starter switches, starter relays, wire harnesses for transmissions, windshield washer nozzles, air conditioner panel switch boards, coils for fuel-related electromagnetic valves, connectors for fuses, horn terminals, insulating boards for electric parts, step motor rotors, lamp sockets, lamp reflectors, lamp housings, brake pistons, solenoid bobbins, engine oil filters, power sheet gear housings, parts for ignition coils, and ignition cases. In addition to those, the moldings have many other applications. In particular, the resin composition of the invention is favorable far box-type moldings, especially for those required to be lightweight, for example, audio trays for CD, and DVD, housings for portable telephones, boards and frames for pocket phone bells, and housings for personal computers, as well as housings for other various appliances and instruments. Specifically, the composition is significantly useful for box-type moldings with thin-wall parts, in which the thin-wall parts having a thickness of at most 1.0 mm account for at least 10. % of the total surface area of the molding. Most preferably, the composition is used for housings for personal

computers.

[0055] Now, the invention is described in sill more detail with reference to the following Examples.

Reference examples:

A-1:

[0056] ε-caprolactam was polymerized in an ordinary manner to prepare pellets of nylon 6. As measured, the relative viscosity of the polyamide was 2.70, the melting point thereof was 222°C, and the terminal amino content thereof was 4.0×10^{-6} equivalents/g.

A-2:

[0057] An equimolar salt of hexamethylenediamine-adipic acid was polymerized in an ordinary manner to prepare pellets of nylon 66. As measured, the relative viscosity of the polyamide was 2.75, the melting point thereof was 262°C, and the terminal amino content thereof was 4.9×10^{-6} equivalents/g.

A-3:

[0058] An aqueous solution of a mixture of hexamethylenediammonium terephthalate (6 T salt) and aminododecanoic acid (solid concentration: 60 % by weight), that had been controlled to have hexamethyleneterephthalamide units in an amount of 50 mol% and dodecamide units in an amount of 50 mol%, was fed into a pressure reactor for polymerization, heated with stirring, and reacted under a water vapor pressure of 19 kg/cm^2 for 1.5 hours. Then, this was gradually degassed over a period of about 2 hours, and further reacted for about 30 minutes in a normal-pressure nitrogen atmosphere. The polyamide resin thus obtained had a relative viscosity of 2.55, a melting point of 283°C, and a terminal amino content of 4.5×10^{-6} equivalents/g.

A-4:

[0059] As in Reference Example 1, ε-caprolactam was polymerized in an ordinary manner, but 0.1 parts by weight of a terminal blocking agent, benzoic acid, was added to 100 parts by weight of the monomer, ε-caprolactam. Pellets of nylon 6 were obtained. As measured, the relative viscosity of the polyamide was 2.70, the melting point thereof was 222°C, and the terminal amino content thereof was 2.1×10^{-6} equivalents/q.

B-1:

[0060] 528 parts by weight of p-hydroxybenzoic acid, 126 parts by weight of 4,4'-dihydroxybiphenyl, 112 parts by weight of terephthalic acid, 864 parts by weight of polyethylene terephthalate having an intrinsic viscosity of about 0.6 dl/g, and 586 parts by weight of acetic anhydride were fed into a reactor equipped with a stirrer and a distillation tube, and polymerized therein. As a result, obtained was a liquid-crystalline resin comprising 42.5 mol% of aromatic oxycarbonyl units, 7.5 mol% of aromatic dioxy units, 50 mol% of ethylenedioxy units, and 57.5 mol% of aromatic dicarboxylic acid units, and having a liquid crystal transition temperature of 184°C. As measured through an orifice of $0.5\ \phi \times 10$ mm at different temperatures at a shear rate of 1,000 sec^{-1}, the melt viscosity of the resin was 30 Pa·s at 247°C, 15 Pa·s at 287°C, and 1 Pa·s at 308°C.

B-2:

[0061] 777 parts by weight of p-hydroxybenzoic acid, 126 parts by weight of 4,4'-dihydroxybiphenyl, 112 parts by weight of terephthalic acid, 519 parts by weight of polyethylene terephthalate having an intrinsic viscosity of about 0.6 dl/g, and 816 parts by weight of acetic anhydride were fed into a reactor equipped with a stirrer and -a distillation tube, and polymerized therein. As a result, obtained was a liquid-crystalline resin comprising 62.5 mol% of aromatic oxycarbonyl units, 7.5 mol% of aromatic dioxy units, 30 mol% of ethylenedioxy units, and 37.5 mol% of aromatic dicarboxylic acid units, and having a liquid crystal transition temperature of 205°C. As measured through an orifice of $0.5\ \phi \times 10$ mm at different temperatures at a shear rate of 1,000 sec^{-1}, the melt viscosity of the resin was 35 Pa·s at 247°C, 20 Pa·s at 287°C, and 2 Pa·s at 308°C.

B-3:

[0062] 907 parts by weight of p-hydroxybenzoic acid, 457 parts by weight of 2,6-hydroxynaphthoic acid, and 872 parts by weight of acetic anhydride were fed into a reactor equipped with a stirrer and a distillation tube, and polymerized therein. As a result, obtained were pellets of a resin with 100 mol% of aromatic oxycarbonyl units, having a liquid crystal transition temperature of 260°C. As measured through an orifice of 0.5 $\phi \times$ 10 mm at different temperatures at a shear rate of 1,000 sec^{-1}, the melt viscosity of the resin was 120 Pa·s at 287°C, and 35 Pa·s at 308°C. However, its melt viscosity could not be measured at 247°C.

[0063] The liquid crystal transition temperature (TN) of the resins was measured, using a micrometer for melting point measurement (from Yanako).

Examples 1 to 9, and Comparative Examples 1 to 12:

[0064] As in Table 1, the polyamide resin (A-1 to A-4) and the liquid-crystalline resin (B-1 to B-3) that had been prepared in the Reference Examples, and the acid anhydride and carbon fibers having a mean length of 6 mm were weighed, each to a predetermined amount, and dry-blended. Using a single-screw (30 mmϕ) extruder, the resulting blends were separately melted and pelletized. The cylinder temperature was as in Table 1, and the number of screw revolutions fell between 30 and 100 rpm. After having been, dried in hot air, the pellets were fed into a Sumitomo Nestal injection molding machine, Promat 40/25 (from Sumitomo Heavy Machine industry), and molded into test pieces in an injection-molding manner. The cylinder temperature and the mold temperature were as in Table 1. These test pieces were tested for their properties, according to the methods mentioned below.

(1) Fluidity:

[0065] Each composition sample was left in the cylinder of the molding machine for a residence time of 20 minutes, and molded into test pieces having a thickness of 0.5 mm and a width of 12.7 mm, at an injection ratio of 99 % and an injection pressure of 500 kgf/cm^2, whereupon the length of the running test piece (the length of the running resin bar) was measured.

(2) Impact Resistance:

[0066] Each test piece with no notch (thickness: 1/8 inches) was subjected to a Charpy impact test according to JIS K6911.

(3) Surface Appearance:

[0067] Square plates of 70 × 70 × 2 mm thick were produced through injection molding, and visually checked as to whether or not their surface was swollen owing to impurities, or yellowed owing to gas generation, or as to whether or not fibers are seen, on their surface. "Good" in Table 1 means that the samples had good surface appearance, while "Bad" therein means that the samples had some surface failures.

(4) Cushion Resin Fluctuation:

[0068] Bending test pieces having a size of 12.7 × 127 × 3.2 mm were molded, according to a molding cycle comprising injection for 5 seconds, cooling for 10 seconds, and an on-standby period of 4 seconds. Twenty cycles were repeated, and the variation in the cushion resin present in the cylinder under pressure was measured for its standard deviation. The cushion resin is meant to indicate the amount of the resin (g) remaining in the cylinder between the tip of the screw and the nozzle, while the resin is molded through the cylinder, and this is represented relative to the position between the nozzle and the screw. For this, the standard was 5 mm. For the cushion resin, the amount of the resin for full charging in the mold plus alpha (+ α) is weighed and charged into the mold (this is for removing molding failures to cause shrinkage cavities in moldings), so that the excess resin is left in the tip of the cylinder. The amount of the excess resin, α, indicates the cushion resin.

(5) Cobwebbing in Molding:

[0069] In test (4), the condition of the resin, running out of the nozzle was checked for the presence or absence of cobwebbing around it. "Yes" in Table 1 means that cobwebbing was seen; and "No" therein means that no cobwebbing was seen.

Table 1

	Polyamide Resin 100 wt.pts.	Liquid-crystalline Resin (wt.pts.)	Acid Anhydride (wt.pts.)	Filler (wt.pts.)	Working Temp. (°C)	Mold Temp. (°C)	Fluidity (mm)	Impact Resistance (kg·cm/cm^2)	Surface Smoothness	Cushion Resin α	Cob-webbing
Example 1	A-1	B-1 (3)	Succinic Anhydride (0.5)	-	250	80	120	6.0	Good	0.09	No
Example 2	A-1	B-2 (3)	Phthalic Anhydride (0.8)	-	250	80	117	5.8	Good	0.11	No
Example 3	A-2	B-1 (3)	Succinic Anhydride (0.5)	-	290	80	131	3.9	Good	0.14	No
Example 4	A-2	B-2 (3)	Succinic Anhydride (0.5)	-	290	80	129	3.8	Good	0.14	No
Example 5	A-3	B-2 (3)	Phthalic Anhydride (0.5)	-	305	80	134	3.2	Good	0.10	No
Example 6	A-1	B-1 (3)	Succinic Anhydride (0.5)	CF (45)	270	80	88	4.2	Good	0.10	No
Example 7	A-1	B-1 (25)	Succinic Anhydride (0.6)	-	270	80	145	4.2	Good	0.16	No
Example 8	A-2	B-3 (3)	Phthalic Anhydride (0.5)	-	290	80	108	2.7	Good	0.21	No
Example 9	A-4	B-1 (3)	Succinic Anhydride (0.3)	CF (45)	270	80	88	4.0	Good	0.10	No

	Polyamide Resin 100 wt.pts.	Liquid-crystalline Resin (wt.pts.)	Acid Anhydride (wt.pts.)	Filler (wt.pts.)	Working Temp. (°C)	Mold Temp. (°C)	Fluidity (mm)	Impact Resistance (kg·cm/cm^2)	Surface Smoothness	Cushion Resin α	Cob-webbing
Compara. Example 1	A-1	-	-	-	250	80	90	4.0	Good	0.25	Yes
Compara. Example 2	A-2	-	-	-	290	80	96	2.2	Good	0.27	Yes
Compara. Example 3	A-3	-	-	-	305	80	101	1.7	Good	0.33	Yes
Compara. Example 4	A-1	-	Succinic Anhydride (0.5)	-	250	80	92	3.5	Bad	0.24	Yes
Compara. Example 5	A-1	B-1 (3)	-	-	250	80	86	3.8	Good	0.16	No
Compara. Example 6	A-1	B-1 (200)	Succinic Anhydride (0.5)	-	250	80	130	1.2	Bad	0.73	No
Compara. Example 7	A-1	B-1 (3)	Succinic Anhydride (7.0)	-	250	80	125	2.0	Bad	0.45	Yes
Compara. Example 8	A-1	-	-	CF (45)	270	80	66	3.0	Bad	0.21	Yes
Compara. Example 9	A-1	B-1 (3)	-	CF (45)	270	80	62	2.6	Good	0.18	No
Compara. Example 10	A-1	-	Succinic Anhydride (0.5)	CF (45)	270	80	67	2.4	Bad	0.22	Yes
Compara. Example 11	A-4	-	-	CF (45)	270	80	67	3.0	Bad	0.22	Yes
Compara. Example 12	A-4	B-1 (3)	-	CF (45)	270	80	64	2.4	Good	0.20	No

[0070] From the data in Table 1 above, it can be seen that each of the polyamide resin compositions embodying the invention has good fluidity even when it is left for a relative long period of residence time in a cylinder of a large-sized molding machine while it is molded, and has good moldability. As to their moldability, the resin compositions embodying the invention are free from significant fluctuation in the amount of the cushion resin remaining in the cylinder, and from cobwebbing around the nozzle through which it runs out. In addition, it can also be seen therefrom that the moldings of the resin compositions embodying the invention all have good mechanical strength as indicated by the impact resistance and have good surface appearance.

Claims

1. A polyamide resin composition comprising 100 parts by weight of a polyamide resin, from 0.01 to 100 parts by weight of a liquid-crystalline resin, and from 0.01 to 5 parts by weight of a polycarboxylic acid anhydride component, at least a portion of which polycarboxylic acid anhydride component is optionally present as units derived from polycarboxylic acid anhydride present in at least one other component of the resin but not then providing a proportion of the said parts by weight content of the other component.

2. A polyamide resin composition according to claim 1, wherein the liquid crystal transition temperature of the liquid-crystalline resin is not higher than the melting point of the polyamide resin.

3. A polyamide resin composition according to claim 1 or claim 2, which further contains a filler in an amount of from 0.05 to 300 parts by weight relative to 100 parts by weight of the total amount of the polyamide resin, the liquid-crystalline resin and the acid anhydride.

4. A polyamide resin composition according to any preceding claim, wherein the melt viscosity of the liquid-crystalline resin is not higher than 50 Pa•s, as measured at a temperature of the melting point of the polyamide resin + 25°C and at a shear rate of 1000 sec^{-1}.

5. A polyamide resin composition according to any preceding claim, wherein the acid anhydride is at least one selected from succinic anhydride, 1,8-naphthalic anhydride, phthalic anhydride and maleic anhydride.

6. A box-type molding with thin-wall parts having a thickness of at most 1mm molded from a polyamide resin composition comprising 100 parts by weight of a polyamide resin, from 0.01 to 100 parts by weight of a liquid-crystalline resin, and from 0.01 to 5 parts by weight of an acid anhydride, wherein the thin-wall parts account for at least 10% of the total surface area of the molding.

7. A polyamide resin composition obtainable by mixing, in molten form, 100 parts by weight of a polyamide resin and from 0.01 to 100 parts by weight of a liquid-crystalline resin, and, in molten or liquid form, from 0.01 to 5 parts by weight of a polycarboxylic acid anhydride.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 3721

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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X : particularly relevant if taken alone
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